PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Cold-Hardening Compositions containing Phenol-Formaldehyde Condensation Products, and a process for making such Compositions

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister, Lucius & Brüning, a body corporate recognised under German law, of Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to compositions which are capable of hardening rapidly in the cold to yield chemically resistant masses, and which contain phenol-formaldehyde condensation products, and to a process for making such compositions.

It has already been proposed to improve the chemical resistance of masses produced by the hardening of compositions capable of hardening rapidly in the cold and prepared from precondensed, liquid phenolaldehyde condensation products and additions of neutral or acid hardeners and fillers, by the addition of neutral aliphatic esters of an inorganic acid having no hardening effect on the condensation product such for instance, as alkyl phosphates. For the same purpose, it has been proposed to add chlorinated aliphatic alcohols, for instance, dichloropropanol, or halogenated aliphatic or aromatic aldehydes or their hydrates. Aromatic esters of inorganic acids such, for instance, as arylalkyl chlorides, also improve the chemical resistance but, in contradistinction to the above mentioned substances, they have a tendency to harden the liquid aldehyde condensation products in the cold. This involves the drawback that the said esters, when mixed with the latter substances, cannot be stored for long periods.

The present invention is based on the observation that a certain group of aromatic compounds has no hardening effect on the liquid formaldehyde condensation products at ordinary temperature, so that these compounds can be stored also in admixture with the said condensation products for long periods before the addition of the powder containing a hardener.

Compositions capable of hardening rapidly in the cold, which have been prepared with addition of those aromatic compounds, yield masses which have a high chemical resistance especially to cold alkali lyes, piperidine, pyridine, pyrrole and other organic bases, as well as to fatty acid esters of aliphatic alcohols. Such compositions can be used, for instance, for jointing brick work or for lining or coating vessels, conduits, pipes or the like, which come into contact with acid liquids or the aforesaid chemical agents.

According to this invention, therefore, compositions capable of hardening rapidly in the cold to yield chemically resistant masses are made by mixing a powder containing a filler and a hardening agent (as hereinafter defined) with a liquid mixture containing a liquid condensation product obtained by condensing in an alkaline medium for formaldehyde and at least one mononuclear monohydric phenol and also containing at least one aryloxy compound obtained by the reaction of a phenol with chlorinated aliphatic alcohol.

Depending on the purpose for which the final hardened masses are to be used, the quantity of the powder may range from about 1—3 parts by weight to every

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1 part by weight of liquid used for making the paste.

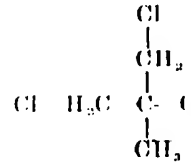
The condensation products of formaldehyde with mononuclear monohydric phenols, for instance, phenol itself (C_6H_5OH), the isomeric cresols or xylenols, and above all commercial mixtures of cresols or of xylenols, are prepared in the usual manner in the presence of an alkaline catalyst, for instance, caustic soda solution, and the proportion of formaldehyde to phenol used advantageously ranges from about 1:1 to about 1.8:1. The preferred proportion ranges from about 1.4:1 to about 1.6:1. In some cases, however, a proportion 1.2:1 may be advantageous.

The preparation of the condensation products from formaldehyde and mononuclear monohydric phenols in an alkaline medium may be carried out, for example, as follows:

55 parts by weight of phenol are introduced into 14 parts by weight of a caustic soda solution of 42 per cent. strength at about 60—70° C. After cooling to about 35—40° C., 100 parts by weight of a formaldehyde solution of 30 per cent. strength are run in, and the whole is maintained at that temperature for about 2—3 days. The whole is then neutralized by the addition of 34 parts by weight of crude hydrochloric acid of 20 per cent. strength, while cooling with ice, the temperature not being allowed substantially to exceed about 40° C. After 3 hours, the weakly acid mixture is allowed to separate into layers, the resin layer is washed with water, while stirring, and renewed separation into layers, and the mixture is adjusted to a pH value of 7—8 by the addition of caustic soda solution.

Especially good results can be obtained by using the aryloxy compound in a proportion ranging from about 1 to 35 per cent. on the weight of the formaldehyde condensation product. Proportions outside these limits are, however, also useful.

The aryloxy-compounds are obtained by condensing at least one monohydric phenol with at least one chlorinated aliphatic alcohol in an alkaline medium. As phenols there may be used, for instance, phenol itself (C_6H_5OH), the isomeric cresols or xylenols, α-naphthol or β-naphthol. As chlorinated aliphatic alcohols there come into consideration, for instance, 1:3-dichloropropanol, epichlorhydrin and tertiary dichloro-isobutyl alcohol of the formula:



Such an aryloxy-compound is obtained, for example, by alkaline condensation of dichloropropanol with phenol according to the empirical equation:

$$C_6H_5OH + CH_2Cl—CH(OH)—CH_2Cl = C_6H_5—O—CH_2—CH(OH)—CH_2Cl + HCl$$

Such aryloxy-compounds are prepared, for instance, by heating for 2 hours under reflux 108 parts by weight of paracresol with 129 parts by weight of dichloropropanol or 92.5 parts by weight of epichlorhydrin and 40 parts by weight of NaOH powder, and distilling the aryloxy-compound formed under reduced pressure.

By the addition of one or more of these aryloxy-compounds to a liquid formaldehyde condensation product of the above kind, liquids are obtained which are used for pasting with the powder in making the compositions capable of hardening rapidly. The masses produced by the hardening of these compositions have an extraordinary chemical resistance which by far surpasses that resulting from the known addition of aliphatic esters alone.

In some cases it may be of advantage to add, besides the above mentioned aryloxy-compounds, neutral aliphatic esters of inorganic acids, which have no hardening effect and which have already been proposed for use as the sole addition. The proportion used range from about 5—25 per cent. on the weight of the formaldehyde condensation product. As additions the following substances come into consideration: Hydrochloric acid esters of aliphatic alcohols or halogenated aldehydes, for example, dichloropropanol, dichlorhydrin or ethylene chlorhydrin; and the corresponding phosphoric acid esters such as triethyl phosphate or trimethyl phosphate.

Moreover, it may be advantageous in some cases to add also aldehydes, for instance, formaldehyde, acetaldehyde or benzaldehyde either alone or mixed with each other. These aldehydes are added in liquid form to the liquid resin mixture, or where obtainable, in the form of powders, such as paraformaldehyde or paraldehyde, to the mixed filler-hardener powder.

In some cases these aldehydes may be added in one and the same batch to the

powder and also to the resin mixture. The quantities of the added aldehydes range, in general, from about 5 to about 10 per cent., calculated on the weight of the formaldehyde condensation product.

The term "hardening agent" or "hardener" is used herein to mean a hardening agent for liquid phenol formaldehyde condensates obtainable by condensation in an alkaline medium of formaldehyde with at least one mononuclear monohydric phenol. As hardening agents of this kind there are used in the present invention agents capable of effecting rapid hardening in the cold, such as acid or neutral persulphates, titanium sulphate, metal dioxides having a neutral reaction to water, such as lead peroxide or manganese dioxide; or aromatic sulphochlorides, such as para-toluene sulphochloride, β-naphthalene sulpho-chloride, or aralkyl chlorides or aralkyl sulphates, such as dichloromethyl metaxylol or dibenzyl sulphate, naphthalene disulphonic acids, and especially 1:5-naphthalene disulphonic acid and it is to be understood that the hardening agents used in the present invention do not include aldehydes. The mixed filler-hardener powder may contain one or more of the above hardening agents in any desired admixture with one another.

The powder also contains one or more inert fillers of the kind known to those skilled in this art, such for instance, as quartz powder, barium sulphate and especially fillers of good thermal conductivity, such as natural or artificial graphite, silicon or silicon compounds such as silicon carbide.

The powder is prepared by simply mixing the ingredients together.

The compositions capable of hardening rapidly in the cold to yield chemically resistant masses are obtained by mixing a powder, containing at least one hardening agent (as hereinbefore defined) and at least one filler, with a liquid containing at least one aryloxy-compound of a monohydric phenol and a chlorinated aliphatic alcohol, and also a liquid condensation product obtained by condensing formaldehyde with a phenol in an alkaline medium, and if desired, containing a neutral aliphatic ester of an inorganic acid.

The composition may be made up in two separate parts which are mixed together immediately before use, one part consisting of a powder containing the hardening agent and the filler and the other part comprising the aryloxy-compound and the liquid condensation product, and if desired, a chlorinated aliphatic alcohol.

The following Examples illustrate the invention, the parts being by weight;

EXAMPLE 1.

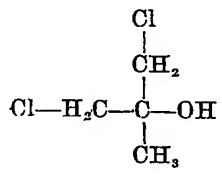
7 parts of finely powdered 1:5-naphthalene disulphonic acid are mixed with 93 parts of heavy spar. The powder thus obtained is pasted with a liquid consisting of 30 parts of a liquid phenolformaldehyde condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and phenol in the ratio of 1.4:1, and 10 parts of the aryloxy-compound prepared by condensing 1:3-dichloropropanol with phenol in an alkaline medium.

EXAMPLE 2.

10 parts of finely powdered para-toluene sulphochloride are mixed with 90 parts of graphite powder of the kind used for carbon electrodes. The resulting powder is pasted with a liquid consisting of 30 parts of a liquid condensation product, pre-condensed in an alkaline medium, from formaldehyde and a commercial xylenol mixture in the ratio of 1.6:1, and 5 parts of the aryloxy-compound obtained by alkaline condensation of epichlorhydrin and para-cresol.

EXAMPLE 3.

6 parts of finely powdered para-toluene sulphochloride and 4 parts of 1:5-naphthalene disulphonic acid are mixed with 90 parts of heavy spar. The resulting powder is pasted with a liquid consisting of 30 parts of a liquid cresol-formaldehyde condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and para-cresol in the ratio of 1.2:1, and 3 parts of the aryloxy-compound obtained by condensing in an alkaline medium β-naphthol with tertiary dichlorisobutanol of the formula:



EXAMPLE 4.

5 parts of 1:5-naphthalene disulphonic acid and 2 parts of β-naphthalene sulphochloride are mixed with 93 parts of artificial graphite powder. The resulting powder is pasted with a liquid mixture consisting of 30 parts of a liquid condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and a commercial xylenol mixture in the ratio of 1.5:1, 3 parts of dichloropropanol and 2 parts of the aryl-

oxy compound obtained by condensing 1:3 dichloropropanol with para-cresol in an alkaline medium.

EXAMPLE 5

10 parts of finely powdered para-toluene sulphochloride are mixed with 90 parts of finely ground calcined electrode carbon. The powder so obtained is pasted with a liquid consisting of 30 parts of a liquid condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and phenol in the molecular ratio of 1.6:1, and 10 parts of the aryloxy compound obtained by condensing 1:3-dichloropropanol with phenol in an alkaline medium.

EXAMPLE 6.

5 parts of 1:5-naphthalene disulphonic acid and 2 parts of β naphthalene sulphochloride are mixed with 93 parts of graphite powder. The powder so obtained is pasted with a liquid consisting of 15 parts of a liquid condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and phenol in the molecular ratio of 1.7:1, 15 parts of a liquid condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and a commercial xylenol mixture in the molecular ratio of 1.8:1, 5 parts of an aryloxy-compound obtained by condensing para-cresol with dichloropropanol in an alkaline medium, and 5 parts of an aryloxy-compound obtained by condensing phenol with epichlorhydrin in an alkaline medium.

EXAMPLE 7.

10 parts of para-toluene sulphochloride are mixed with 90 parts of heavy spar. The powder so obtained is pasted with a liquid consisting of 10 parts of a liquid condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and phenol in the molecular ratio of 1.6:1, 20 parts of a liquid condensation product, pre-condensed in an alkaline medium and prepared from formaldehyde and a commercial mixture of isomeric cresols in the molecular ratio of 1.4:1, 3 parts of an aryloxy-compound obtained by condensing in an alkaline medium phenol with tertiary dichlorisobutyl alcohol, and 2 parts of triethyl phosphate.

EXAMPLE 8.

100 parts of a liquid condensation product produced by alkaline condensation from formaldehyde and phenol (C_6H_5OH) in the molecular ratio of 1.3:1 are mixed with 15 parts of the aryloxy-compound obtained by reacting epichlorhydrin with para-cresol in an alkaline medium, 5 parts of benzaldehyde and 10 parts of glycol-chlorhydrin. The mixture obtained is used for making a paste with a powder consisting of 90 parts of artificial graphite powder, 5 parts of paraformaldehyde and 5 parts of 1:5-naphthalene disulphonic acid. With 100 parts of the powder about 80 parts of the above liquid are required.

Our co-pending Application No. 24874/50 (Serial No. 702,112) describes and claims the manufacture of compositions capable of hardening rapidly in the cold to yield chemically resistant masses, which comprise at least one hardening agent for liquid phenol formaldehyde condensates, at least one filler, furfurol and a liquid condensation product obtained by condensing formaldehyde with at least one mononuclear monohydric phenol in an alkaline medium, and which may also contain at least one substance capable of increasing the chemical resistance of the hardened phenol-formaldehyde resin; and it is to be understood that the use of furfurol in the compositions of the present invention is expressly excluded.

Subject to the foregoing disclaimer what we claim is:—

1. A composition capable of hardening rapidly in the cold to yield chemically resistant masses, which composition comprises at least one hardening agent (as hereinbefore defined), at least one filler, at least one aryloxy-compound of a monohydric phenol and a chlorinated aliphatic alcohol, and a liquid condensation product obtained by condensing in an alkaline medium formaldehyde with at least one mononuclear monohydric phenol.

2. A composition as claimed in Claim 1, which also contains at least one aliphatic ester of an inorganic acid.

3. A composition as claimed in Claim 1 or 2, which also contains at least one aldehyde such, for instance, as formaldehyde, acetaldehyde, benzaldehyde, paraformaldehyde or paraldehyde.

4. A composition as claimed in Claim 1, 2 or 3, wherein the liquid condensation product has been obtained by condensing in an alkaline medium formaldehyde with phenol itself (C_6H_5OH).

5. A composition as claimed in Claim 1, 2 or 3, wherein the liquid condensation product has been obtained by condensing in an alkaline medium formaldehyde with a commercial mixture of xylenols.

6. A composition as claimed in Claim 1, 2 or 3 wherein the liquid condensation product has been obtained by condensing in an alkaline medium formaldehyde with para-cresol.

7. A composition as claimed in any one of Claims 1—6, wherein the liquid con-

densation product has been obtained by condensing the formaldehyde with the phenol in a molecular ratio ranging from about 1:1 to about 1.8:1, and preferably from about 1.4:1 to about 1.6:1.

8. A composition as claimed in any one of claims 1—7, wherein the proportion of the aryloxy-compound ranges from about 15—35 per cent. on the weight of the formaldehyde condensation product.

9. A composition as claimed in any one of claims 1—8, wherein the aryloxy-compound has been obtained from para-cresol and 1:3-dichloropropanol.

10. A composition as claimed in any one of claims 1—9, wherein the hardening agent is 1:5-naphthalene disulphonic acid or para-toluene sulphochloride.

11. A composition as claimed in any one of claims 1—10, wherein the filler is heavy spar or graphite powder.

12. A composition capable of hardening rapidly in the cold to yield a chemically resistant mass, which composition has been made substantially as described in any one of Examples 1—8 herein.

13. A process for making compositions capable of hardening in the cold to yield a chemically resistant mass, which comprises mixing at least one hardening agent (as hereinbefore defined) with an inert filler and mixing the resulting powder with a liquid containing at least one aryloxy-compound of a monohydric phenol and a chlorinated aliphatic alcohol and also containing a liquid condensation product obtained by condensing in an alkaline medium formaldehyde with at least one mononuclear monohydric phenol.

14. A process as claimed in Claim 13, wherein the liquid condensation product has been obtained by condensing the formaldehyde with the phenol in a molecular ratio ranging from about 1:1 to about 1.8:1, and preferably from about 1.4:1 to about 1.6:1.

15. A process as claimed in claim 13 or 14, wherein the liquid condensation product has been obtained by condensing, in an alkaline medium formaldehyde with phenol itself (C_6H_5OH).

16. A process as claimed in claim 13 or 14, wherein the liquid condensation product has been obtained by condensing in an alkaline medium formaldehyde with a commercial mixture of xylenols.

17. A process as claimed in claim 13, or 14, wherein the liquid condensation product has been obtained by condensing in an alkaline medium formaldehyde with para-cresol.

18. A process as claimed in any one of claims 13—17, wherein the proportion of the aryloxy-compound ranges from about 15—35 per cent. on the weight of the formaldehyde condensation product.

19. A process as claimed in any one of claims 13—18, wherein the aryloxy-compound has been obtained from para-cresol and 1:3-dichloro-propanol.

20. A process as claimed in any one of claims 13—19, wherein the liquid also contains at least one aliphatic ester of an inorganic acid.

21. A process as claimed in any one of claims 13—20 wherein the liquid also contains at least one aldehyde in the liquid state, such, for example, as formaldehyde, acetaldehyde and benzaldehyde.

22. A process as claimed in any one of claims 13—21, wherein the hardening agent is 1:5-naphthalene disulphonic acid or para-toluene sulphochloride.

23. A process as claimed in any one of claims 13—22, wherein the filler is heavy spar or graphite powder.

24. A process as claimed in any of the claims 13—23, wherein the powder also contains paraformaldehyde and/or paraldehyde.

25. A process for making a composition capable of hardening rapidly in the cold to yield a chemically resistant mass, conducted substantially as described in any one of Examples 1—8.

26. A modification of the composition claimed in any one of claims 1—12, in which the composition is made up in two separately packed parts to be mixed together prior to use, one part consisting of a powder containing the hardening agent and the filler and the other part comprising the aryloxy-compound and the liquid condensation product, and if desired, a chlorinated aliphatic alcohol.

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